PREPARATION AND DEVELOPMENT

OF EPITATCTIC GaAs FILMS - PHASE I

Final Report

by

D. Walsh
Professor, Department of Physics, McGill Industrial Research
McGill University, Montreal, Quebec

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS FILE NUMBER	:	20SU.23440-1-9112
DSS CONTRACT SERIAL NUMBER	:	OSU81-00436
CANMET PROJECT NUMBER	:	450.202
CANMET SCIENTIFIC AUTHORITY	:	Dr. S.M. Ahmed

JAN 2 0 1984

MICROMEDIA

DATE: Sept. 1983

This report should be cited as Contract Report No.: OSU81-00436

SUBCONTRACT WITH ENERGY MINES and RESOURCES

(Account No. 236-54)

Preparation and characterization of epitactic GaAs films for photoelectrochemical applications.

Final Report
March 15, 1983

Attention : Dr. S.M. Ahmed

The single crystal epitactic GaAs films were grown on semiinsulating GaAs (100) substrates. The induction furnace was a single zone cold-walled quartz type held at 625°C at 0.3 Torr pressure. Various graphite pedestals were employed but best reproducible results were achieved with graphite coated with a glassy carbon layer. The substrate temperature was read at the start of each run using an infra-red detector and the thermocouple embedded in the pedestal calibrated accordingly. The chemical reaction consists of the reduction by Pd-purified H_2 of Trimethyl (gallium (TMG), whose vapour pressure is controlled by use of a thermo-electric cooler, to CH_4 and Ga, the latter reacting with arsine to give GaAs. Total gas flow rates, which are determined by electrically controlled mass flow valves, are $\sim$ 20 cc/min. and the corresponding growth rate at 625°C is $\sim$ 1μ/hr. All the epilayers were a few microns thick and after growth suitable samples were either cut, sand-blasted or etched into the usual configuration for Hall measurements. Ohmic contacts were made using a 12% Ge-Au alloy for n-type GaAs and Zn followed by pure Au for p-type GaAs. Hall coefficients and mobilities were obtained in a typical low temperature dewar although all measurements quoted here are at 300°K ; magnetic fields were set at 4KG and the corresponding electric field was less than 1 V cm^{-1}. Photoluminescence spectra were also recorded in the range 2°K - 20°K and were similar to that reported by us recently (J. Phys. C. : Solid State, 15, 7043-7048, 1982). All undoped epilayers are compensated, usually n-type with $N_A + N_D$ in the 10^{17}/c.c. range.

All p-type GaAs were grown using both DMZ and DEZ as dopants ; however, the latter is more convenient due to its higher vapour pressure. For DMZ at -10°C and a Ga/Zn ratio of 5, μ_p = 77 $cm^2v^{-1}s^{-1}$ and N_A = 1.4 10^{18} cm^{-3} .

For DEZ at -10°C a Ga/Zn ratio of 300 gave μ_p = 102 $cm^2V^{-1}s^{-1}$ and N_A = 210^{17} cm^{-3} . In all cases crystal quality was excellent. H_2Se was used as a dopant for all n^+ type GaAs. Using an As/Se ratio of 5450 we obtained $N_D = 10^{18}$ cm^{-3} and μ_n = 2136 $cm^2V^{-1}s^{-1}$; a ratio of 1700 gave $N_D = 10^{19}$ cm^{-3} with μ_n = 660 $cm^2V^{-1}s^{-1}$.

Listed in the Table below are the samples which have been delivered to EMR ; the electrical properties have been determined by Hall-coefficient measurements on each sample.

Type	Mobility cm^2/Vs	Carrier concentration cm^{-3}	Resistivity ohm-cm	epilayer thickness μ
n	2909	9.6×10^{16}	0.0222	1.5
p	68	3×10^{18}	0.0299	5.1
p	153	2×10^{18}	0.0183	-
p	32	2.8×10^{17}	0.6467	10.4
n	2136	1.3×10^{18}	0.0017	5.3
n	2550	1.2×10^{18}	0.0022	4.4
n	657	5.6×10^{18}	0.017	4.3

GROWTH APPARATUS

REACTOR:
- cold wall with and without water jacket.
- quartz tubing 50/52 and 100/102 mm (ID/OD).
- stainless steel end flanges with O-ring seals on quartz tubing.

PEDESTAL:
- Graphite SiC coated pedastal.
- Graphite amorphous carbon (glassy carbon) coated pedastal.
- Molybdenium 99.999% pure pedastal.
- supported by thermal couple (TC) in a S.S. sheath.

TEMPERATURE:

Growth:
- controled by a Barber Colman model 560 temp.controller ($\pm 1°C$).
- temperature readout from TC embedded in pedastal.
- controller temperature calibrated by infrared detector.

Heat Source:
- induction heating (Lepel R.F. furnace).
- temperature of OM controlled by thermal electric cooler ($\pm 1°C$).

GAS CONTROL:

Organometallic:
- H_2 carrier gas through OM bottle, Mass Flow Meter 0-10 ccm (±.001)

Hydrogen mixture:
- arsine in hydrogen: 0-100 ccm (±.01).
- hydrogen selenide: 0-100 and 0-1 ccm.

PRESSURE:
- reduced pressure maintained by a 19cfm rotary pump.
- normal growth pressure : .300 to .500 torr (±.001).
- pressure read by Capacitance Manometer (±.001 torr).
- molecular sieve, before pump, prevents back diffusion of oil.

OTHER FEATURES:
- all tubing 1/4 S.S., welded joints and swage lock fittings.
- system monitored by He leak detector.
- Ar gas maintianed in system after growth.

$2\,Ga(CH_3)_3 + 3\,H_2 \rightarrow 2\,GaAs + 6\,CH_4$

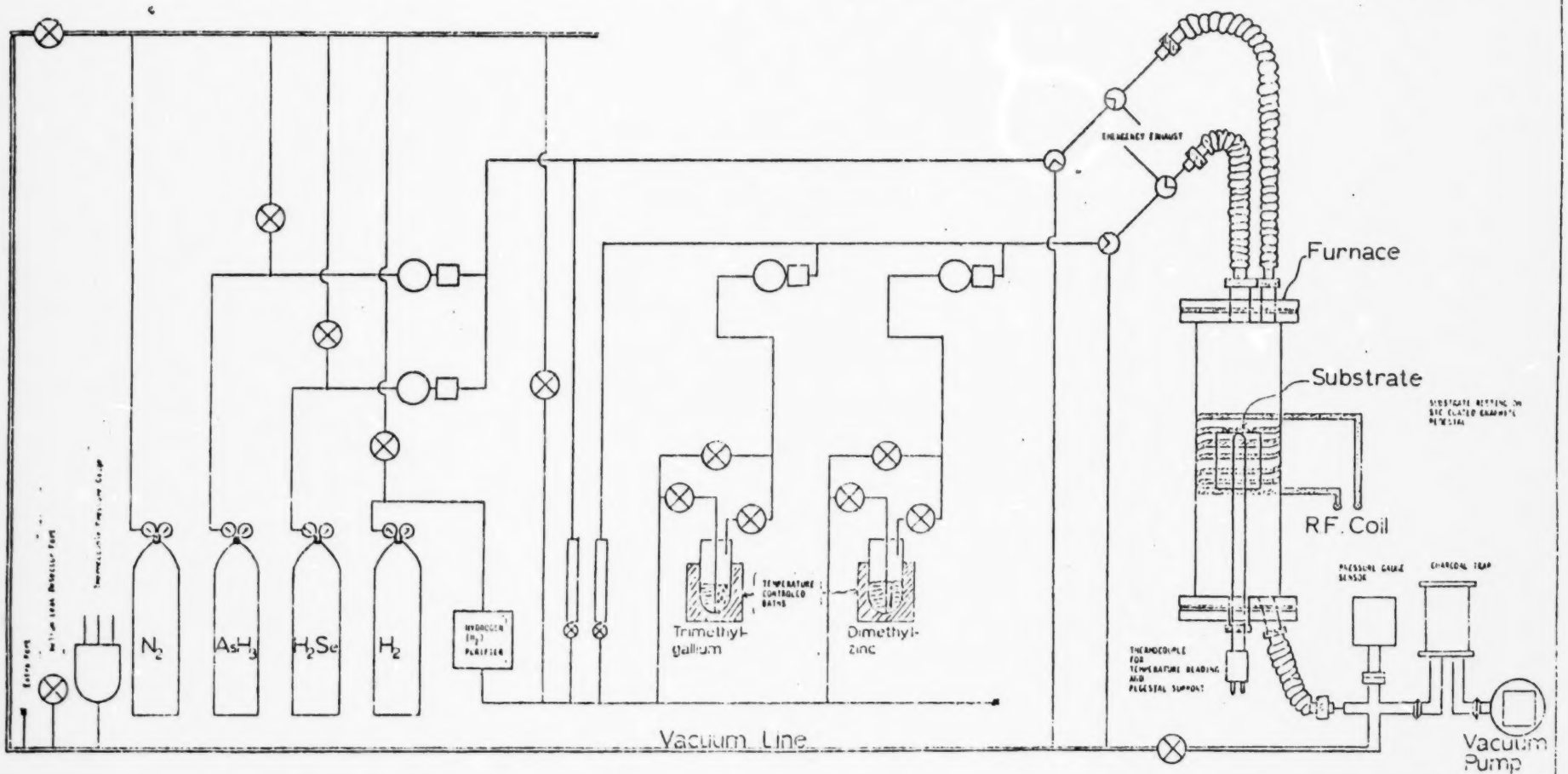
$2\,Ga + 2\,AsH_3 \rightarrow 2\,GaAs + 3\,H_2$

Dopants :

$Zn(CH_3)_2$

H_2Se

SCHEMATIC DIAGRAM OF ORGANO-METALLIC CHEMICAL VAPOUR DEPOSITION (OMCVD) SETUP (MOVPE)



STANDARD RUN

CRYSTAL PREPARATION:
- polished.
- thoroughly degreased.
- etch: $H_2SO_4:H_2O_2:H_2O$ (4:1:1) for 15 min @ 22 C.
- rinsed in ultra pure water (18megΩ) and methanol.
- blown dry with pure N_2.

PRESSURE:
- maintained at ~~.45~~ .3 torr (±.05).

FLOW:
- typical total flow rate ~~45~~ 30 ccm.

TEMPERATURE:
- surface of substrate at ~~610~~ 605°C ±1°C (read by pyrometer).
- thermal couple: 645°C stable to ±1°C.
- organometalics: -10°C (±.1) for TMG.
  -10°C (±.1) for DEZ.

GROWTH RATE:
- 1 μ/hr at ~~610~~ 605°C.

THICKNESS:
- measured by weight, verified by SEM.

SUBSTRATE:
- GaAs N,P type semi-insulating (Cr doped or undoped)
- Germanium
- Saphire
- dimension: max 500 mm^2, typical 200 mm^2.

PEDESTAL:
- Graphite amorphous carbon (glassy carbon) coated.

CRYSTAL CHARACTERISTICS

GROWTH MORPHOLOGY:
- mirror finish with growth rate of .5 to 3 μ/hr.

OHMIC CONTACTS:
- Au 88%-Ge 12% for n-type.
- Au-Zn-Au for p-type.
- Au for n^+ and p^+.
- evaporated from tungsten bolt at 10^{-5} torr.
- anneal at 450°C in N_2 atm.

ELECTRICAL MEASUREMENTS:
- electrical mobility and Hall coefficient obtained using van der Pauw type geometry.
- six ears:
  - two for current
  - two each for Vh and Vx.

ELECTRICAL CHARACTERISTICS:
- for undoped (n-type) GaAs epilayers.
  - mobility: 2500-4000
  - resistivity: .001-.01
  - carrier conc. (N_D-N_A): 2×10^{16}
  - total impurities (N_D+N_A): 5×10^{16}
  - thickness: undoped- 4-9 μ.

J. Phys. C: Solid State Phys., 15 (1982) 7043–7048. Printed in Great Britain

Metallic impurity donor band in compensated n-type GaAs

D Walsh, A Poirier, C Christoforou† and J Auclair
Rutherford Physics Building, McGill University, Montreal, Quebec, Canada H3A 2T8

Received 8 February 1982, in final form 14 June 1982

Abstract. The resistivity, Hall coefficient and photoluminescence of compensated n-GaAs grown epitaxially by MOVPE establish the existence of a metallic donor impurity band whose mean separation from the conduction-band edge is 5 meV. Using a two-band model, we obtain uniquely the desired majority and minority impurity concentrations from the Hall coefficient experimental data.

1. Introduction

It is well known that for n- and p-type semiconducting crystals compensation reduces electronic screening (Fritzsche 1980, Mott and Davies 1980, Durkan *et al* 1968) with the result that a metallic phase is absent even though the majority impurity concentration may greatly exceed that given by the Mott criterion (Mott 1956). Varying degrees of compensation of the uncompensated crystal have been achieved, by neutron activation for instance; the resulting random minority impurity distribution introduces a random fluctuating electric field in the crystal and at low temperatures the electrical conductivity is small, being governed by a phonon-assisted hopping process in the impurity band. On the other hand, the electrical conductivity of a number of semiconducting crystals can be described by a two-band model in which an impurity metallic-like band is well separated from the corresponding conduction- or valence-band edge (Conwell 1956, Vul *et al* 1971)‡. Invariably, due to the lack of a mature technology at the time, the latter materials were relatively impure compensated semiconducting crystals, in which, however, during crystal growth the minority and majority impurity atoms were uniformly distributed resulting in a fairly uniform overlap of majority impurity wavefunctions. Currently, we are developing a high-efficiency photovoltaic cell using metal–organic vapour-phase epitaxy (MOVPE) of GaAs—a relatively new semiconductor technology with great potential (Dupuis and Dapkus 1978). The undoped epitaxial GaAs crystals are of compensated n-type with a metallic impurity band separated from the conduction-band edge by approximately the binding energy of the isolated donor level, the evidence for which is developed below.

† Present address: Physics Department, University of Waterloo, Ontario, Canada.

‡ The properties of samples 10 and 11 of Vul *et al* (1971) are consistent with this model, although the authors did not apply it.

0022-3719/82/347043 + 06 $02.00 © 1982 The Institute of Physics

2. Measurement and analysis

The epitaxial n-type GaAs was grown on a semi-insulating Cr-doped (100) GaAs substrate (SI GaAs) in a single-zone cold-wall induction furnace at 625 °C and 0.3 Torr pressure (Walsh and Auclair 1982). The reaction consists of the reduction by Pd-purified H_2 of trimethyl gallium (TMG), whose vapour pressure is controlled by means of a thermoelectric cooler, to CH_4 and Ga, the latter reacting with arsine to give GaAs. Total gas flow rates, which are determined by electrically controlled mass flow valves are

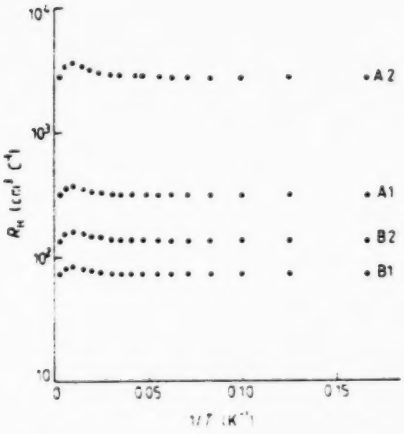


Figure 1. Hall mobility, μ_H, against T for the four n-type GaAs samples listed in table 1. The experimental error is ±5%.

≈20 cm^3 min^{-1}, and the growth rate is ≈1 μm h^{-1}. The samples used in this study were epitaxial n-type GaAs, a few microns thick, on SI GaAs cut (after epitaxial growth) for Hall measurements into a rectangular shape, 4 × 1.5 mm^2, with two ears protruding from one of the long edges and one facing ear placed symmetrically on the opposite edge. Ohmic contacts were made using a 12% Ge–Au alloy. Hall coefficients and mobilities were obtained in a typical He dewar over the temperature range 4–300 K. The magnetic field as 4 kG while the electric field was less than 1 V cm^{-1}. All photoluminescence spectra were recorded in the liquid He temperature range in a back-scattering configuration using a krypton-ion laser, and low power plus a defocused cylindrical lens to avoid overheating (Ashen *et al* 1975). The data were spectrally analysed with a 1M double monochromator, GaAs photomultiplier tube and standard photon-counting equipment.

Table 1. Impurity concentrations in cm^{-3} of epitaxial n-type GaAs. $K = N_A/N_D$ and $\alpha = \mu_c/\mu_i$.

Sample	$N_D - N_A$	N_D	N_A	K	α
A1	2.0×10^{16}	8.0×10^{16}	6.0×10^{16}	0.75	2.18
A2	2.25×10^{15}	6.89×10^{16}	6.66×10^{16}	0.97	2.99
B1	8.7×10^{16}	1.3×10^{17}	4.3×10^{16}	0.33	2.12
B2	4.7×10^{16}	7.8×10^{16}	3.1×10^{16}	0.40	2.25

Figure 1 shows the Hall mobility, μ_H, for four n-type GaAs samples whose electron concentrations vary from 2×10^{15} to 9×10^{16} cm^{-3}. However, the crystals are heavily compensated with donor concentrations, N_D, and acceptor concentrations, N_A, as listed in table 1. The results indicate the presence of a metallic impurity donor band with concentrations corresponding to the intermediate impurity range discussed by Alexander and Holcomb (1968); see also the discussion in Keyes (1968). Figure 2 shows the constancy of the electron concentration at low T with the well known maximum in R_H

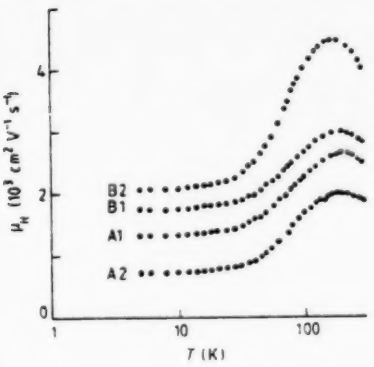


Figure 2. Hall coefficient, R_H, against T^{-1} for the four n-type GaAs samples listed in table 1. The experimental error is ±5%.

for a two-band model, when $\mu_i n_i = \mu_c n_c$, where μ_i and μ_c are the electron mobilities in the impurity and conduction bands respectively and n_i and n_c are the corresponding carrier concentrations. The photoluminescence intensity of sample A_2 in figure 3, which shows the presence of a donor impurity band, whose average separation from the conduction-band edge is 5 meV, is consistent with this interpretation†. For an isolated

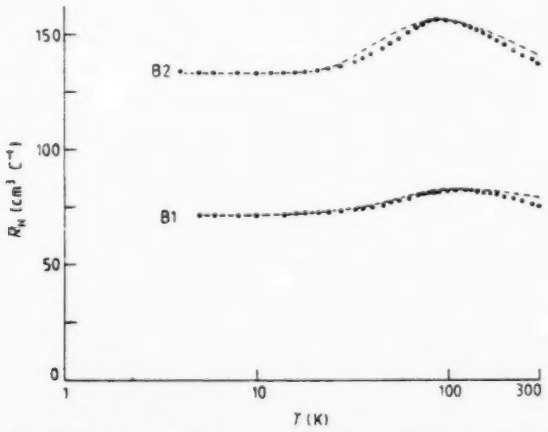


Figure 3. Laser-induced photoluminescence of sample A_2 at 8 K using 5 mW, defocused, with $\lambda = 6764$ Å. Relative photon counts are independent of power level and laser wavelength. The arrow identifies the metallic impurity donor band (IDB) and the energy gap E_g is equal to E_c in the text. The number in parentheses at the foot of the trace multiplies the vertical scale.

† A preliminary resistivity measurement of one sample showed a metallic impurity band down to the lowest temperature achieved, 70 mK.

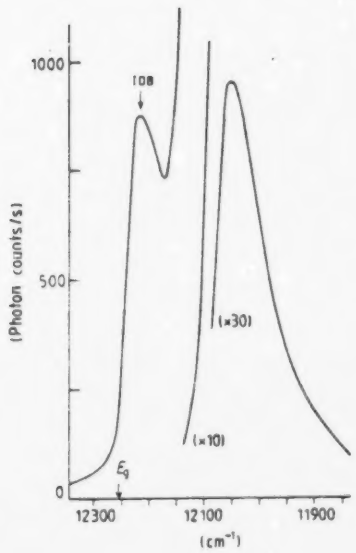


Figure 4. Comparison, for samples B1 and B2, between equation (2) using the values of α and K given in table 1 and the corresponding experimental Hall coefficients. The experimental error is ±5%. The broken curve shows the theoretical result.

impurity it is the free-to-bound donor transition. The average binding energy for the donor band of sample A1 was also found to be 5 meV; however, when the electron concentration exceeded 10^{18} cm^{-3} the donor impurity band merged with the conduction band in addition to some expected band-gap narrowing (Abram *et al* 1978).

Due to the presence of the donor impurity band, the electron mobility does not show the usual $T^{3/2}$ law of ionised impurity scattering below 80 K. Consequently, the Falicov–Cuevas mobility expression for a compensated semiconductor (Falicov and Cuevas 1967) is not suitable in its usual form to determine N_A and N_D from the measured Hall coefficient and mobility.

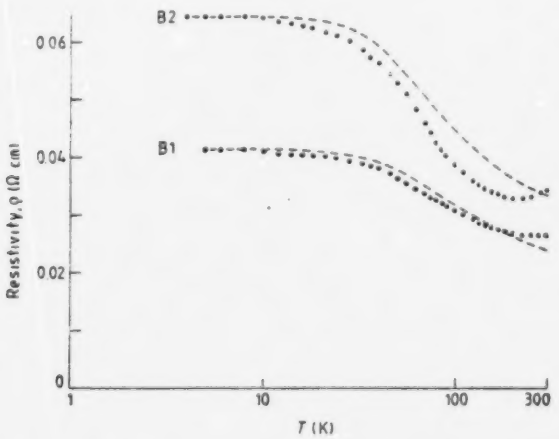


Figure 5. Comparison, for samples B1 and B2, between equation (3) using the values of α and K given in table 1 and the corresponding experimental resistivities. The experimental error is ±5%. The broken curve shows the theoretical result.

For a two-band model R_H is given by

$$R_H = (n_i\mu_i^2 + n_c\mu_c^2)/e(n_i\mu_i + n_c\mu_c)^2. \tag{1}$$

The corresponding Hall factors are taken to be 1. Due to intraband scattering the temperature dependence of the mobility will be minimised. Thus we assume that $\alpha = \mu_c/\mu_i$ is approximately constant, and R_H becomes

$$R_H = (n_i + n_c\alpha^2)/e(n_i + n_c\alpha)^2. \tag{2}$$

Similarly the resistivity, ρ, becomes

$$\rho = [e\mu_i(n_i + n_c\alpha)]^{-1} \tag{3}$$

where μ_i is determined from the low-T data according to the equation $R_H(4\,\mathrm{K}) = \rho(4\,\mathrm{K})\mu_i$. It can be shown that the following relation exists between the experimental values for the Hall coefficients and α:

$$4R_H^{max}/R_H(4\,\mathrm{K}) = (1 + \alpha)^2/\alpha \tag{4}$$

where R_H^{max} is the maximum in R_H. At the temperature corresponding to the maximum in R_H we have $n_i/n_c = \alpha$ and we can determine the compensation $K = N_A/N_D$ uniquely using the charge-neutrality equation

$$N_A + N_D\left\{\left[1 + \tfrac{1}{2}\exp\left(\frac{E_D - E_F}{kT}\right)\right]^{-1} - 1\right\} + 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}\exp\left(\frac{E_F - E_c}{kT}\right) = 0 \tag{5}$$

where $N_D - N_A$ is determined directly from the Hall measurements and we define E_D, E_F, E_c to be the donor binding energy, the Fermi energy and the band-gap energy, respectively, and $m^* = 0.068\,m_0$ is the effective mass, where m_0 is the free-electron mass.

We have found theoretically that the Fermi level remains in the donor band for only a limited temperature range and consequently, for convenience, we assume the width of band is negligible with a binding energy of 5 meV. The carrier concentration ratio n_i/n_c is strongly dependent on the binding energy for a fixed K over the temperature range 0 to 20 K. At higher temperatures the Fermi level E_F is far from the donor impurity band and the ratio n_i/n_c depends only weakly on the binding energy. It is interesting to note that if the temperature corresponding to the maximum in R_H is sufficiently high, reasonable values for N_A and N_D can still be determined without an accurate knowledge of the binding energy.

The experimental Hall coefficient R_H and resistivity ρ are very well reproduced by equations (2) and (3), respectively, knowing α from (4) and K from the condition $n_i/n_c = \alpha$ at the temperature corresponding to the maximum in R_H. Table 1 gives the pertinent parameters for the four samples, while figures 4 and 5 show the close agreement between theory and experiment for samples B1 and B2. The results for samples A1 and A2 are similar.

3. Conclusion

We have established by transport and optical methods for compensated n-GaAs the existence of a metallic donor impurity band whose average separation from the conduction-band edge is 5 meV. The majority and minority impurity concentrations are

determined uniquely from the Hall coefficient experimental data using a two-band model. The corresponding parameters as determined by the Falicov–Cuevas formula agree with those in table 1 to within 50%. By making the simple assumption that α is a constant over the temperature range considered, we find that the resistivity and Hall coefficient measurements are indeed very well reproduced by the two-band model.

The second photoluminescence peak of figure 3 at 27 ± 1 meV below E_c corresponds to the free- to-bound-acceptor transition. It indicates that the dominant acceptor impurity is *C* whose binding energy, E_B, equals 26 meV, although, due to the donor–acceptor tail in the photoluminescence, Mg ($E_B = 28.4$ meV) cannot be ruled out entirely. The major donor impurity is unknown. Impurity concentrations in GaAs obtained by VPE can be decreased by changing the growth rate, but for many high-technology applications a low growth rate is preferable. Consequently, the purity of TMG (and probably AsH_3 also) must be improved if the potential of the MOVPE technology is to be fully realised.

Acknowledgments

The authors wish to thank L Fraas Chevron Research Co., Richmond, and W Stutius, Xerox Palo Alto Research Center, for their valuable assistance on MOVPE techniques, L M Falicov, University of California, Berkeley, for a brief but informative discussion on impurity bands, J O Strom-Olsen, McGill, for his assistance with the $^3He/^4He$ dilution refrigerator, and NSERC of Canada for financial assistance in the form of a Strategic Energy Grant and a Postgraduate Scholarship (AP).

References

Abram R A, Rees G J and Wilson B L H 1978 *Adv. Phys.* **27** 799
Alexander M N and Holcomb D F 1968 *Rev. Mod. Phys.* **40** 815
Ashen D J, Dean P J, Hurle D T J, Mullin J B, White A M and Green P D 1975 *J. Phys. Chem. Solids* **36** 1041
Conwell E M 1956 *Phys. Rev.* **103** 51
Dupuis R D and Dapkus P D 1978 *Appl. Phys. Lett.* **32** 473
Durkan J, Elliott R J and March N H 1968 *Rev. Mod. Phys.* **40** 812
Falicov L M and Cuevas M 1967 *Phys. Rev.* **164** 1025
Fritzsche H 1980 *Phil. Mag.* B **42** 835
Keyes R W 1968 *Rev. Mod. Phys.* **40** 829
Mott N F 1956 *Can. J. Phys.* **34** 1356
Mott N F and Davies J H 1980 *Phil. Mag.* B **42** 845
Walsh D and Auclair J 1982 *J. Appl. Phys.* submitted
Vul B M, Zavaritskaya E I, Voronova I D and Rozhdestvenshaya N V 1971 *Sov. Phys.–Semicond.* **5** 829

POOR

QUALITY

ORIGINAL